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DEVELOPMENT OF ETHANOL GAS SENSORS USING TERNARY METAL OXIDE THICK FILMS

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ABSTRACT

Screen printing was used to successfully create a thick film of SnO2: ZnO: CuOternaty oxide. The formation of nanocomposite material from this thick film was confirmed by XRD and SEM. According to XRD analysis, the structure of SnO2 was orthrorobhmic, ZnO was hexagonal, and CuO was monoclinic, with an average crystallite size in the nano range. The particle size was larger than the crystallite size on average. The TCR was found to be negative, indicating the semiconductor behavior of the prepared thick film.

It was discovered that thick films made of the ternary oxides SnO2: ZnO: CuO responded better at 200^0 C and when exposed to ethanol gas. The sensitivity to ethanol gas of a thick film made of ternary metal oxide was 82.15 percent when the gas concentration and operating temperature were, respectively 1000 ppm and 200^0 C. The film showed 72.72 percent sensitivity to ethanol gas at a gas concentration of 500 ppm and an operating temperature of 200^0 C. Similarly, the film has a sensitivity of 60.68 percent at 100 ppm gas concentration and an operating temperature of 200^0 C

KEYWORDS: thick film of SnO2: ZnO: CuOternaty oxide, XRD and SEM. According to XRD analysis

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Original Article

1. INTRODUCTION

Despite substantial measures taken to control land pollution and water pollution, populated areas are severely affected. Air is a mixture of nitrogen and oxygen as main constituents with other gases in small proportions. It also contains fog and other liquid particles, smoke, dust and other solid particles etc. An increase in proportion of those constituents beyond the particular limits leads to pollution.

Modern gas composition evaluation is executed using state-of-the-art analytical equipment which includes chromatography mixed with mass spectrometry, flame ionization, picture ionization and electron seize gas chromatography detectors.

Those classical analytical devices are especially accurate and reliable devices, capable of locating even lines of pollution in combos and with lifetimes in the variety of a few years, however, their obstacles are an excessive initial cost, high protection charges, size and weight, excessive energy intake, the want for certified personnel and a comparably low time-resolution. A fuel sensor or chemical sensor is a device that can capture and process specific alerts generated and reproducible interactions with the gasoline/vapour molecules.

As a result of the importance of gases in environmental control or dangerous emissions, our society requires gas sensors for domestic, automotive, and industrial statistics applications. As a result, the main reasons for

the need for gas sensors are the monitoring of environmental pollutants and the control of their emission. Thus, the most recent Solid state gas sensors (SGS) are based on changes in the physical and/or chemical properties of their sensing materials when exposed to various gas atmospheres. Although there are numerous materials used to implement these devices, this work will focus on those with semiconductor properties, specifically those containing SnO2, ZnO, and CuO.

2. MATERIAL AND METHODOLOGY

This work concentrates on the study of thick film of SnO2: ZnO: CuO ternary oxide. SnO2: ZnO: CuO nano composites were prepared by mechanical milling method. The ratios of base material SnO2 (80%), dopant ZnO (10%) and CuO (10%) weight were taken and nano composites were prepared by mechanical milling using mortar pestle. The thick films of nano composites were prepared by screen printing method on glass substrate.

2.1 Preparation of Active Powder as a Functional Material

The active SnO2: ZnO: CuO powder ratio as functional material to organic part was kept constant at 70:30. SnO2: ZnO: CuO accounted for 70% of the total. To make the paste, the organic part contains ethyl cellulose (8%) as a temporary binder and 92 percent butyl carbitol acetate (BCA liquid, Merck, Munchen, C10H20O4, BP 245OC) as a vehicle. BCA was added in small amounts, drop by drop, to achieve the desired viscosity and thixotropic properties of the paste.

2.2 Fabrication of Thick Film Resistors

The various steps of fabrication of the thick film resistors of SnO_2: ZnO: CuO are described in the following sections.

2.2.1 Substrate Cleaning

The glass substrates used for the deposition of thick film resistors via screen printing were first cleaned with a soap solution. They were also cleaned with chromic acid to remove finger prints and other impurities from the substrates. Finally, all of the substrates were washed several times with distilled water and then with acetone. Finally, the substrates were dried using an infrared lamp.

2.2.2 Paste Formulation

The SnO2: ZnO: CuO powder was thoroughly mixed and crushed in an acetone medium using a mortar and pestle. During the mixing process, BCA was added drop by drop to achieve the desired paste viscosity. The paste should be thixotropic in order to print through a screen on a substrate.

2.2.3 Screen Printing

The screen-printing of the active powder paste was done in three steps. For screen printing, a nylon screen (140S, 355 mesh counts/cm) was chosen. Using a standard photolithography technique, the required mask (2.00 x 1.25 cm) was created on the screen. Using a mask, the formulated paste was printed on Glass substrates (2.5x1.25 cm). The printed samples were dried for 45 minutes under an IR lamp to evaporate BCA before being fired at an optimised temperature in a 1.5 to 2 hour time temperature profile.

2.2.4 Firing / Sintering

The dried SnO2: ZnO: CuO thick film samples were fired in a muffle furnace at 400℃ for 2 hours (including the time required to reach the peak firing temperature and then maintaining a constant temperature for 30 minutes at the peak value and decreasing to reach room temperature). The rate of cooling was set at 25℃/min. These samples were used to investigate

various characterizations, including structural, electrical, and gas sensing properties.

2.3 Experimental Procedure

SnO2: ZnO: CuO thick films were prepared by screen printing and fired at 400oC, as previously discussed. Attempts are made to investigate the electrical and structural properties of thick films fired at 400oC. The gas sensing properties of SnO2: ZnO: CuO films fired at 400oC were investigated. These properties are discovered to be functions of the material's operating temperatures, non-stoichiometry, gas concentration, type of gas, and grain size. The results are presented in the following sections.

3. RESULT AND DISCUSSIONS

3.1 Structural Characterization by XRD, SEM

The structural characteristics of SnO_2: ZnO: CuO thick films were studied using XRD and surface morphology using SEM. The standard screen printing technique was used for deposition of film firing at 400°C. The XRD spectrum of SnO_2: ZnO: CuO thick films fired at 400°C is shown in Figure 1.

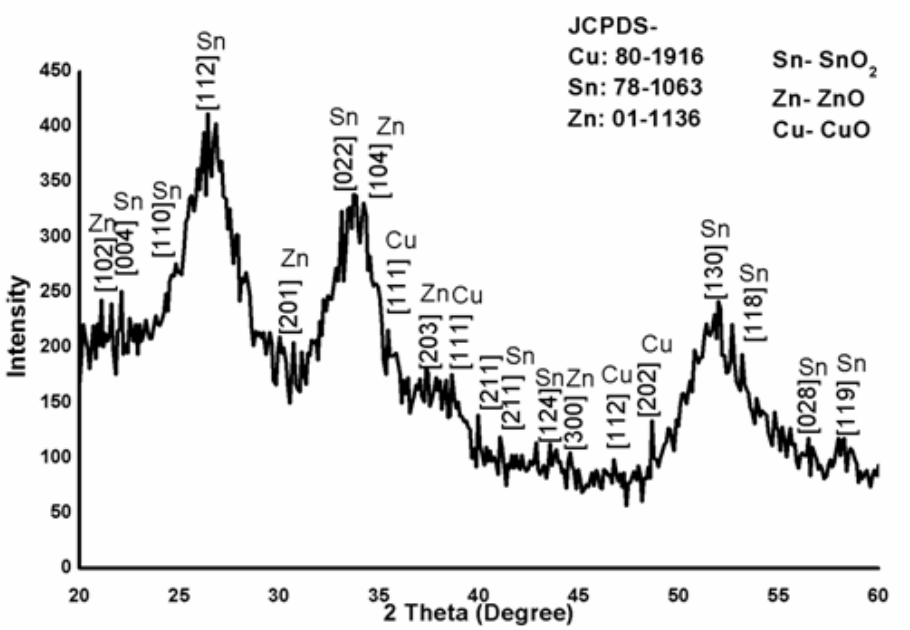


Figure 1: XRD Spectrum of SnO_2: ZnO: CuO Thick Films Fired at 400°C.

It was found that the structure of SnO_2 was orthorhombic, ZnO was hexagonal and CuO was monoclinic structure by comparing hkl parameter with JCPDS Card 78-1063, 01-1136 and 80-1916. XRD confirmed that prepared thick film material was of crystalline nature, prominent peak was at 26.378 which indicates [112] for SnO_2. The maximum intensity of prominent peak shows better crystallinity.

The calculations from XRD pattern and using Debye-Scherrer equation, yielded average crystalline size (D) as 2mm.

3.2 Scanning Electron Microscopy Analysis of Sno2: Zno: Cuo Thick Films

The SEM technique was used to study the morphology of the formed materials as shown in figure 2.

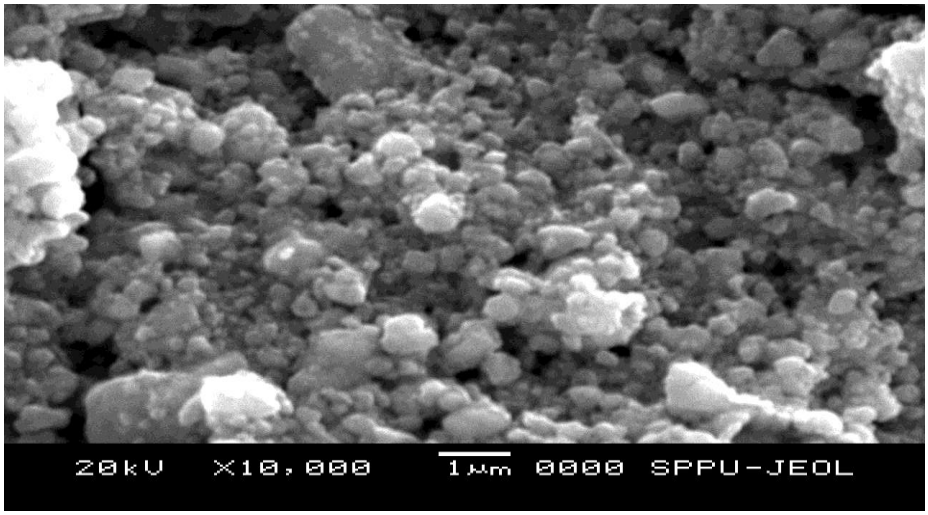


Figure 2: SEM of ZnO: CuO: SnO_2 Thick Film.

The particles are visible in small spheres. The white, gray white and gray brown areas were SnO_2, ZnO and CuO, respectively.

3.3 Electrical Characterization of Zno: Cuo: Sno_2 Thick Film at Cooling

The relationship between temperature and resistance of ZnO: CuO: SnO_2 thick film is shown in Fig.3. With decrease in temperature, the conductivity was showing negative temperature coefficient (NTC) of resistance. Hence, the film was of semi conducting material.

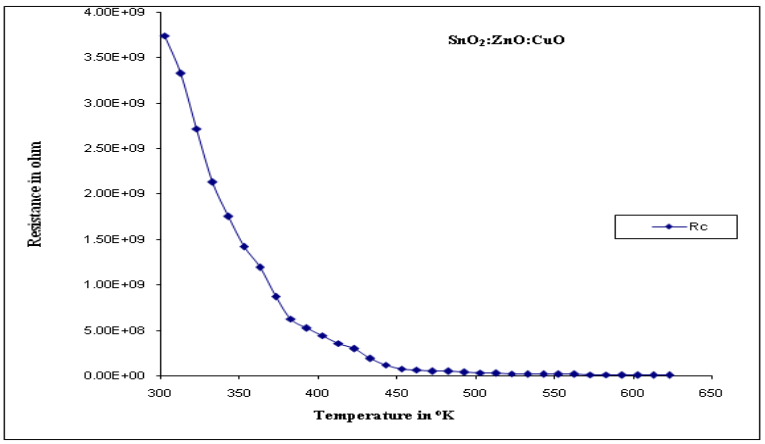


Figure 3: The Relationship Between Temperature and Resistance of Zno: Cuo: Sno_2 Thick Film.

The graph of log R versus a reciprocal of absolute temperature is shown in figure 4.

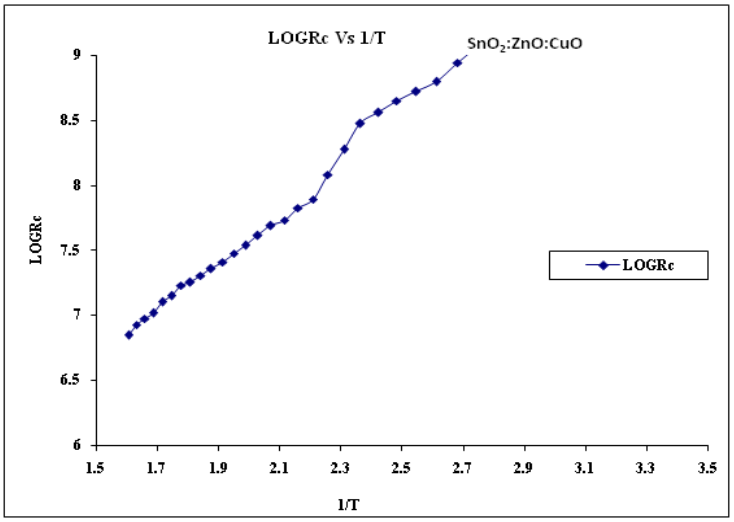
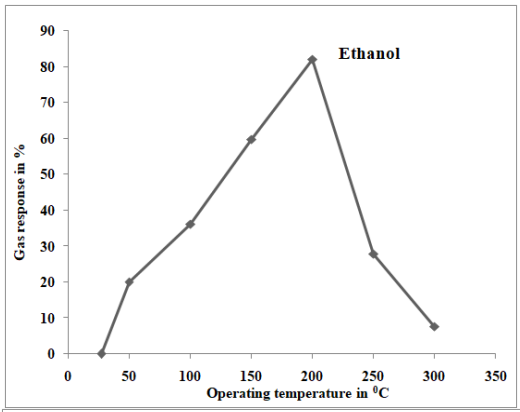


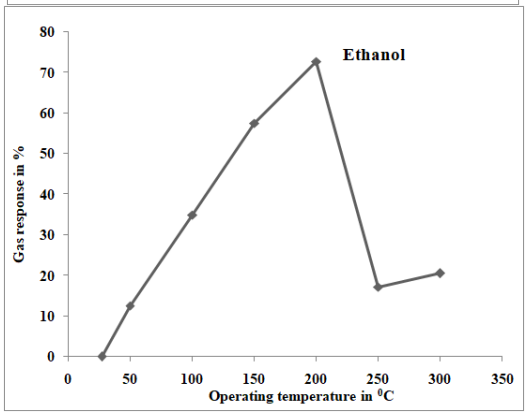
Figure 4: The Relationship Between R and Reciprocal of Absolute Temperature.

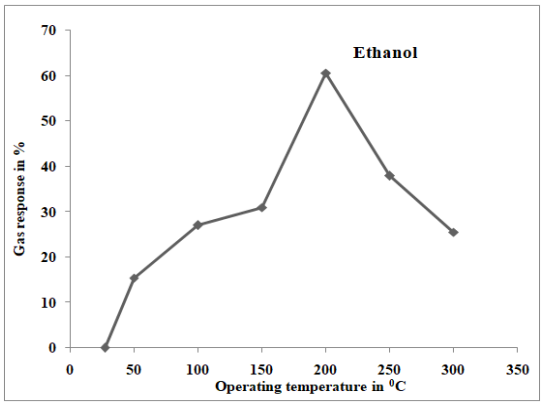
For thickness of 92µm of sample the resistivity, temperature coefficient of resistance (TCR) and activation energy of SnO2: ZnO: CuO thick films was calculated using the relation, and found that resistivity was 1.072 x 105Ω/m. Temperature coefficient of resistance was -0.01022/°C and activation energy for low temperature and high temperature region were 0.30155 eV and 0.28810 eV, respectively.

3.4 Gas Sensing Studies

The thick film SnO2: ZnO: CuO was exposed to ethanol gas at 200^0 C)at various concentration viz., 1000, 500 and 100 ppm. The gas response (sensitivity) has been noted. The results are given in figure 5.







(a) at 1000 ppm, (b) at 500 ppm and (c) at 100 ppm

Figure 5: Sensitivity of SnO_2: ZnO: CuO Thick Film to Ethanol Gas at 200^0 C and Various Concentrations.

The combined response of the thick film of SnO_2: ZnO: CuO was exposed to ethanol gas at 200^{0}C at various concentrations is shown in figure 6.

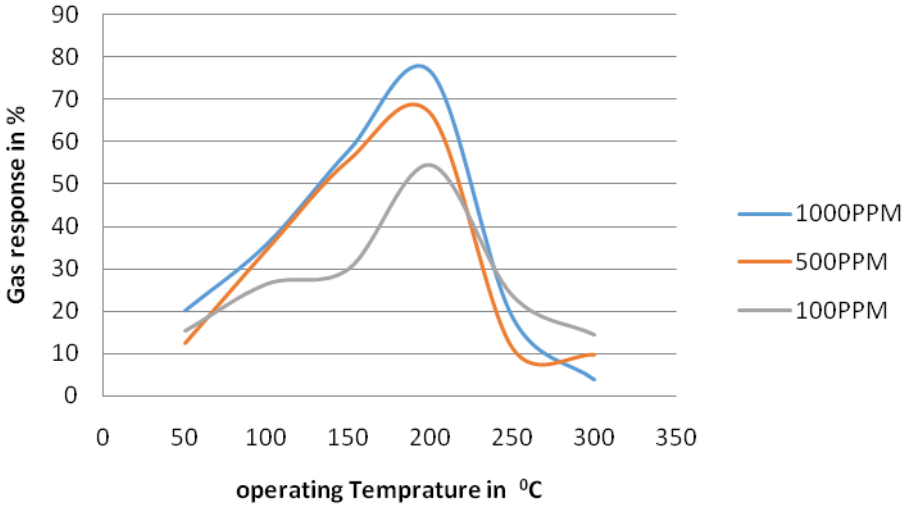


Figure 6: The Combined Response of the Thick Film of SnO_2: ZnO: CuO.

The thick film of SnO_2: ZnO: CuO resulted 82.15 %, 72.72% and 60.68% sensitivities, at 200^{0}C temperature with various concentrations viz., 1000ppm, 500 ppm and 100 ppm, respectively.

3.5 Ethanol Gas Response Study

The sensor's gas sensing performance was investigated by measuring the conductance change of the sensing film in the presence and absence of ethanol gas. The target gas ethanol interacted with the surface of the SnO2: ZnO: CuO thick film and adsorbed oxygen ions on the surface and caused a change in the material's charge carrier concentration. The change in charge carrier concentration caused the resistivity to change. An n-type semiconductor was one in which the majority of charge carriers were electrons, and conductivity increased as it interacted with the reducing gas. Conversely, an oxidizing gas served to deplete the sensing layer of charge carrying electrons, which decreased the conductivity.

In oxide-based materials, the gas sensing mechanism was surface controlled, with grain size, surface states, and oxygen adsorption all played important roles. In the case of ternary oxides (CuO: ZnO: SnO2), a larger surface area meant more adsorption desorption sites and thus increased sensitivity.

4. CONCLUSIONS

Screen printing was used to successfully create SnO2: ZnO: CuOternaty oxide thick films. The obtained materials were heat treated at temperatures of 200^0 C. The formation of SnO2: ZnO: CuO nano composite material was confirmed by XRD and SEM. In XRD, the structures SnO2 (orthrorobhmic), ZnO (hexagonal), and CuO (monoclinic) were observed, and the average crystallite was obtained in the nano range. The particle size was larger than the crystallite size on average. The TCR was found to be negative, indicating the semiconductor behavior of the prepared thick film.

Thick ternary oxide SnO2: ZnO: CuO films respond better at 200^0 C. The thick SnO2: ZnO: CuO film was exposed to ethanol gas. It was discovered that as the concentration of ethanol gas increases, so did the gas response of the film at high temperatures. The sensitivity of the film was 82.15 percent at an operating temperature of 200^0 C and a gas concentration of 1000 ppm. That of was 72.72 at an operating temperature of 200^0 C and 500 ppm concentration. Similarly, it was 60.68 percent at an operating temperature of 200^0 C and concentration of 100 ppm.

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